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Diastereoselective synthesis of a resolved secondary arsine complex: asymmetric synthesis of (R)-$(-)_{589}$-ethylmethylphenylarsine

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Abstract

The reaction of $[R\text{-}(R^*,R^*)]\text{-}(+)_{589}\text{-}[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(NCMe)]PF_6$ with $(\pm)$-AsHMePh in boiling methanol yields crystalline $[R\text{-}[(R^*)\text{-}(R^*,R^*)]\text{-}(+)_{589}\text{-}[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(AsHMePh)]PF_6$, optically pure, in ca. 90% yield, in a typical second-order asymmetric transformation. This complex contains the first resolved secondary arsine. Deprotonation of the secondary arsine complex with $KOBu^t$ at $-65\,^\circ C$ gives the diastereomerically pure tertiary arsenido-iron complex $[R\text{-}[(R^*),(R^*,R^*)]]\text{-}[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4\text{-}(PMePh)_2\}FeAsMePh]\cdot thf$, from which optically pure $[R\text{-}[(S^*),(R^*,R^*)]]\text{-}(+)_{589}\text{-}[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(AsEtMePh)]PF_6$ is obtained by reaction with iodoethane. Cyanide displaces (R)-$(-)_{589}$-ethylmethylphenylarsine from the iron complex, thereby effecting the asymmetric synthesis of a tertiary arsine, chiral at arsenic, from $(\pm)$-methylphenylarsine and an optically active transition metal auxiliary.

Introduction

The stereoselective alkylation of a tertiary arsenido-metal group in a chiral complex provides a potential route to the asymmetric synthesis of tertiary arsines, chiral at arsenic. Uni- and poly-tertiary arsines chiral at arsenic ($E_{inv} > 160$ kJ mol^{-1}) [1*] will exist as stable enantiomers or diastereomers of potential use as stereospecific chelating agents for "soft" metal atoms and ions [2,3]. Depending upon the substituents, terminal tertiary arsenido-metal groups are pyramidal and electronegative ($M\text{–}AsR_2$) [4] or planar and electropositive ($\overline{M}\text{=}\overset{+}{As}R_2$) [5]. In earlier work, we showed that the tertiary phosphido-iron group in (R^*,R^*)-$(\pm)$-$[(\eta^5$-

* Reference number with asterisk denotes a note in the list of references.

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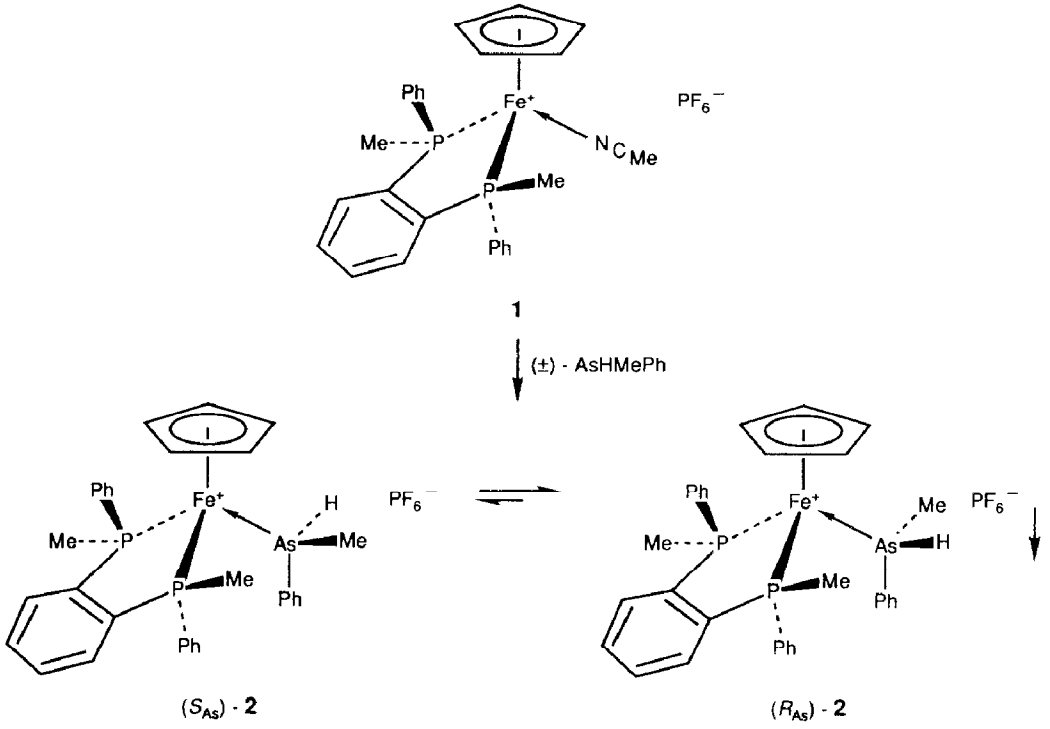
C_5H_5){1,2-C_6H_4(PMePh)$_2$}FePMePh] · thf (E_{inv} ca. 60 kJ mol^{-1}) is alkylated stereospecifically with iodoethane at −95 °C to give the corresponding tertiary phosphine complex in > 99% enantiomeric excess [6,7]. Here we describe our results concerning the stereoselective coordination of (±)-methylphenylarsine to the optically active auxiliary [*R*-(*R**,*R**)]-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe]$^+$ and the subsequent conversion of the resolved secondary arsine in the complex into a resolved form of (±)-ethylmethylphenylarsine.

Results and discussion

Optically pure [*R*-(*R**,*R**)]-(+)$_{589}$-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(NCMe)]-PF_6 (**1**) reacts with one equivalent of (±)-AsHMePh in boiling methanol to give optically pure [*R*-[(*R**),(*R**,*R**)]]-(+)$_{589}$-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe-(AsHMePh)]PF_6, (R_{As})-**2** [8*], in ca. 90% yield, in a typical second order asymmetric transformation (Scheme 1). The crystalline compound is air-stable in the solid state. This is the first example of a complex that contains an optically active secondary arsine. The ^{1}H NMR spectrum of (R_{As})-**2** in dichloromethane-d_2 is consistent with the structure proposed, although the compound slowly decomposes in this solvent with epimerization at arsenic to give (S_{As})-**2** with (R_{As})-**2**/(S_{As})-**2** = 2/1 at equilibrium, along with a 2/1 mixture of unidentified by-products. In Table 1, the ^{1}H NMR data for (R_{As})- and (S_{As})-**2** are presented, together with the corresponding data for [*S*-[(*R**,*R**),(*R**)]]-(−)$_{589}$- and [*S*-[*R**,*R**),(*S**)]]-(−)$_{589}$-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(PHMePh)]PF_6, (S_p)-**5** and (R_p)-**5**, respectively.



Scheme 1

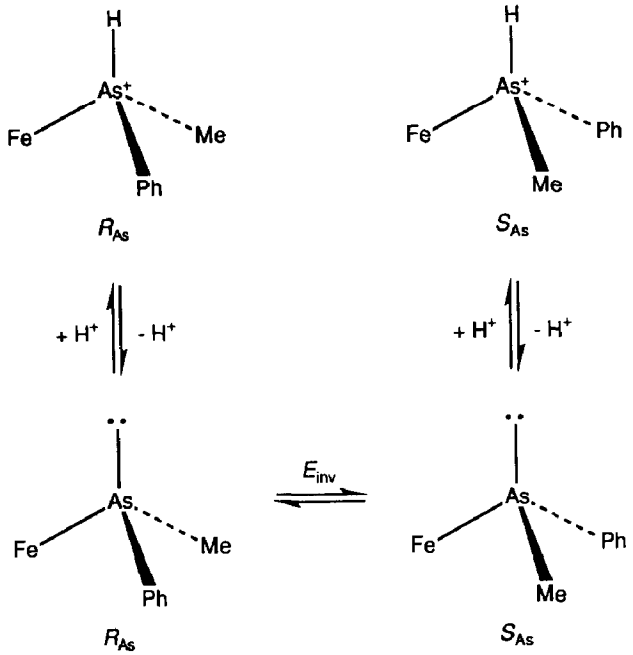
Table 1

Selected ^{1}H NMR data for the complexes $[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(ERMePh)]PF_6$ [a]

Complex	ER	δ(EH)	δ(EMe)	δ(PMe)	δ(PMe)	δ(C_5H_5)
(R_{As})-**2**	AsH	3.28 m	0.58 d	1.83 d	2.28 d	4.34 t
(S_{As})-**2** [b]	AsH	3.39 m	1.46 d	2.21 d	2.35 d	4.31 t
(R_{As})-**4**	AsEt		1.06 s	2.12 d	2.28 d	4.18 t
(S_{As})-**4**	AsEt		0.54 s	2.14 d	2.42 d	4.17 t
(R_p)-**5** [c]	PH	4.65 dm	0.64 dd	1.60 d	2.23 d	4.39 q
(S_p)-**5**	PH	4.83 dm	1.55 dd	2.20 d	2.32 d	4.36 q
(R_p)-**6**	PEt		1.40 d	2.07 d	2.32 d	4.10 q
(S_p)-**6**	PEt		0.64 d	2.09 d	2.45 d	4.10 q

[a] Spectra recorded in CD_2Cl_2 at 20 °C with chemical shifts quoted relative to internal Me_4Si. [b] Observed as minor component of ca. 3/1 mixture of (R_{As})-**2**/(S_{As})-**2** when (R_{As})-**2** was prepared in acidified methanol. [c] Data for epimers of **5** and **6** taken from refs. 6 and 7.

The secondary phosphine complexes have known structures based upon the X-ray crystal structure analysis of $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}$-Fe(PHMePh)]$PF_6 \cdot 0.5CH_2Cl_2$ [6]. The rates of decomposition and epimerisation of (R_{As})-**2** in dichloromethane are reduced by the addition of small quantities of aqueous hydrochloric acid. In hot methanol-d_4, (R_{As})-**2** dissolves without decomposition, but with epimerization at arsenic to give an equilibrium mixture of epimers with (R_{As})-**2**/(S_{As})-**2** = 2/1 at 20 °C. If the methanol solution containing the equilibrium mixture is carefully diluted with diethyl ether, pure (R_{As})-**2** crystallizes in ca. 90% yield. The behaviour of (R_{As})-**2** in solution is consistent with dissociation of the AsH proton followed by inversion and reprotonation of the pyramidal arsenic



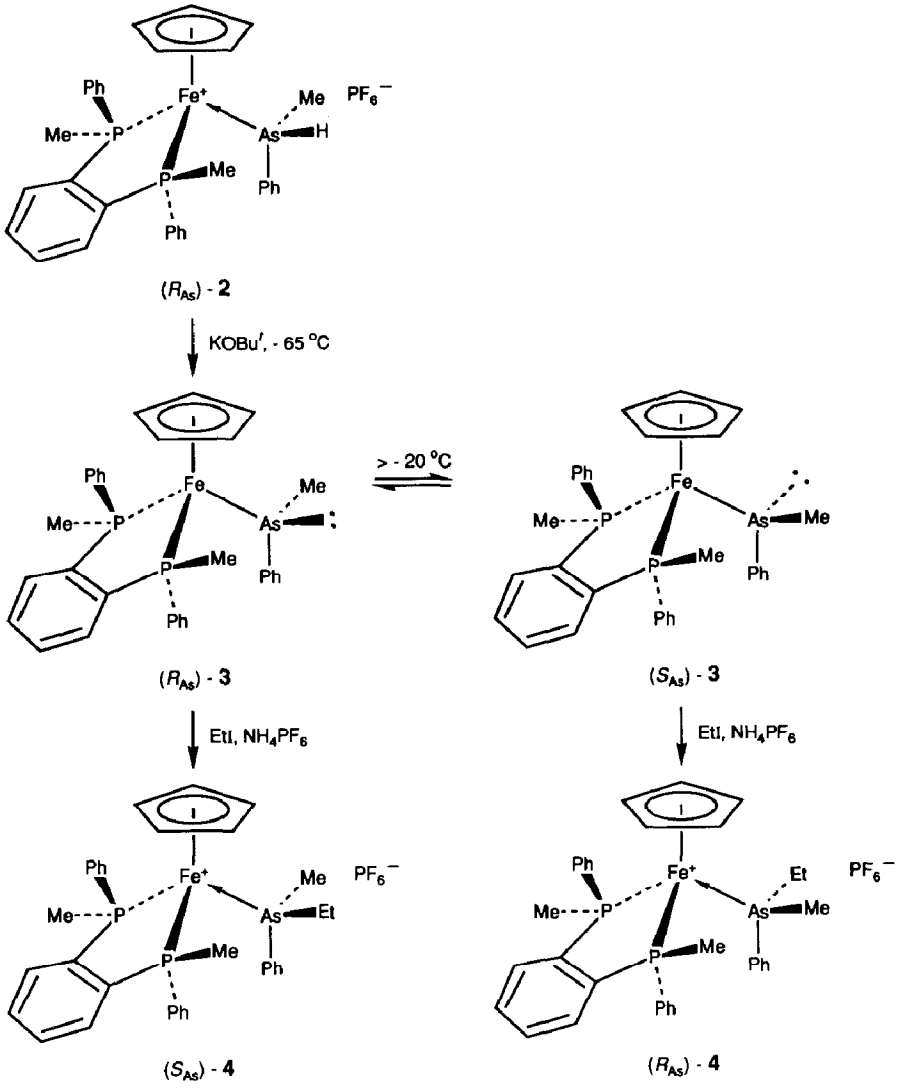
Scheme 2

stereocentre in the tertiary arsenido-iron intermediate (Scheme 2). In dichloromethane, the diastereomeric intermediates apparently react with the solvent in their equilibrium concentrations. As a precedent for this behaviour, dichloromethane reacts with a secondary phosphido-rhenium complex to give a chloromethylphosphine derivative [10]. The acidity of the arsenic proton in (R_{As})-**2** conforms with the properties of protonated tertiary arsines (with which the complex is formally analogous); unlike tertiary phosphines, tertiary arsines are extremely weak bases – liquid hydrochloric acid is required to protonate trimethylarsine [11].

Deprotonation of (R_{As})-**2** with KOBu^t in tetrahydrofuran at $-65\,^\circ$C is stereospecific giving diastereomerically pure (R_{As})-**3**. Upon warming the solution, the pyramidal arsenic stereocentre in the deprotonated complex undergoes inversion to give (S_{As})-**3**. The rate of inversion of the arsenic stereocentre can be monitored at $20\,^\circ$C by ^{1}H NMR spectroscopy in toluene-d_8 solution. Under these conditions, (R_{As})-**3**:(S_{As})-**3** = 2/1 at equilibrium, which corresponds to $\Delta G^{\neq}$ (293 K) = 91.2 ± 2.2 kJ mol^{-1} [12*] ($t_{1/2}$ ca. 70 min). Thus, the pyramidal methylphenylarsenido-iron group in this complex is considerably more stable to inversion than the methylphenylphosphido-iron group, which has $\Delta G^{\neq}$ (278 K) = 58.8 ± 1.2 kJ mol^{-1} for the inversion barrier in an analogous complex [6]. The arsenido-iron complex could not be isolated in an optically pure state because of arsenic stereocentre inversion under the recrystallization conditions. Mixed alkyl aryl substituted tertiary arsines themselves have much higher barriers to pyramidal inversion than similar tertiary phosphines, viz. E_{inv} > 170 kJ mol^{-1} (AsR_3) [13] and E_{inv} 120–140 kJ mol^{-1} (PR_3) [14]. For both arsines and phosphines, the barriers are lowered by electronegative substituents, which stabilize planar transition states due to $n \rightarrow \pi^*$ interactions from the central atoms to the electronegative groups [13,14]. In the present system, the chiral transition metal auxiliary appears to exert a strongly electronegative influence on the arsenic group, thus facilitating inversion of the group via the planar transition state $\overline{Fe} = \overset{+}{As}MePh$.

Diastereoselective synthesis of (R)-(−)$_{589}$-ethylmethylphenylarsine

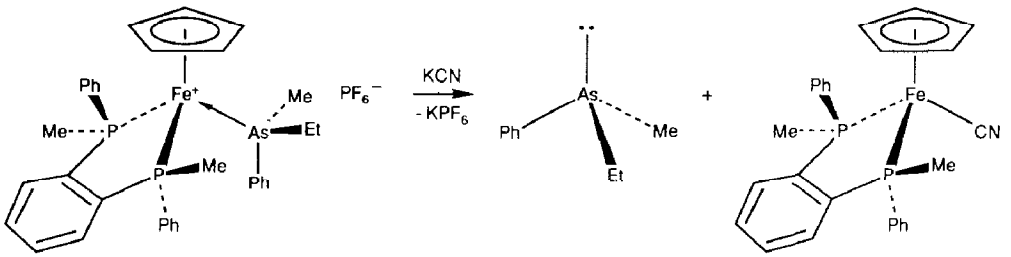
Treatment of (R_{As})-**3**, which was generated in situ from (R_{As})-**2** and KOBu^t in tetrahydrofuran at $-65\,^\circ$C, with iodoethane (at the same temperature), followed by work-up of the reaction mixture with aqueous NH_4PF_6, gave diastereomerically pure (S_{As})-**4**, $[\alpha]_D$ +403° (CH_2Cl_2), in 87% yield (Scheme 3). The reaction is completely stereoselective at $-65\,^\circ$C with retention of absolute configuration at arsenic. The stereochemical assignment for (S_{As})-**4** is based upon the similarity of the ^{1}H NMR chemical shifts for the PMe and AsMe protons in the complex compared to those for the analogous tertiary phosphine complexes (R_p)- and (S_p)-**6** (Table 1). Proton NMR data for the phosphine complexes are also presented in Table 1. Further confirmation of the identity of (S_{As})-**4** was obtained by preparing an equimolar mixture of (R_{As})- and (S_{As})-**4** from **1** and (±)-AsEtMePh, and then separating the mixture by fractional crystallization; the ^{1}H NMR spectrum of (S_{As})-**4** obtained in this manner in dichloromethane-d_2 was identical to that of the compound obtained from the asymmetric synthesis. Moreover, there was a consistency between the ^{1}H NMR data for (S_{As})-**4** and the data for the precursor complex (R_{As})-**2**. When (R_{As})-**3** was generated from (R_{As})-**2** in tetrahydrofuran at $20\,^\circ$C, and the solution was treated with iodoethane within 10 min of the addition of the base, an (S_{As})-**4**/(R_{As})-**4** = 7/1 mixture of products resulted, reflecting



Scheme 3

predominantly kinetic control of the alkylation due to the relatively low rate of epimerization of the arsenic stereocentre in the intermediate (R_{As})-**3**. Ethylation of (R_{As})-**3** generated at 20 °C after 12 h gave the thermodynamic mixture (S_{As})-**4**/(R_{As})-**4** = 2/1.

This work has shown that the asymmetric synthesis of a chiral tertiary arsine in a chiral metal complex is feasible. The acidity of a coordinated secondary arsine in a cationic complex coupled with the relatively low inversion barrier of the conjugate base, a pyramidal tertiary arsenido-metal complex, permits the diastereoselective synthesis of a secondary arsine complex by a second-order asymmetric transformation. Moreover, low temperature deprotonation of a coordinated secondary arsine (or phosphine [7]) is stereospecific with retention of configuration at arsenic to give a pyramidally stable tertiary arsenido-metal intermediate that can be alkylated with total stereoselectivity in a subsequent reaction. If the stereospecific displacement of



(S_{As})-4 (R_{As})-7 8

Scheme 4

the resolved chiral tertiary arsine from the complex could be achieved an optically pure tertiary arsine could be synthesized from a racemic secondary arsine by this route. In the present system (R)-$(-)_{589}$AsEtMePh ((R_{As})-**7**), $[\alpha]_D$ $-2.0°$ (c 0.751, Et_2O) {Lit: $[\alpha]_D$ $-3.05°$ (c 0.369, Et_2O) [20]}, was displaced from (S_{As})-**4** by cyanide in boiling aqueous methanol with concomitant formation of $[R$-$(R^\star,R^\star)]$-$(+)_{589}$-$[(\eta^5$-$C_5H_5)\{1,2$-$C_6H_4(PMePh)_2\}FeCN]$ (**8**) (Scheme 4). We are presently seeking alternative ligands that will allow displacement of tertiary arsines under milder conditions.

Experimental

Reactions were performed under argon by Schlenk techniques. Solvents were dried and purified by distillation under argon. Proton NMR spectra were recorded in dichloromethane-d_2, unless indicated otherwise, on a Bruker CXP 200 spectrometer at 293 K; chemical shifts are reported as δ values relative to internal Me_4Si. Optical rotations were measured with a Perkin–Elmer Model 241 polarimeter in a 1-dm cell at 294 K. Elemental analyses were performed by staff within the Research School of Chemistry.

The compounds (±)-methylphenylarsine [15], (±)-ethylmethylphenylarsine [16], $[S$-$(R^\star,R^\star)]$-(+)-1,2-phenylenebis(methylphenylphosphine) [17], and bromodicarbonyl(η^5-cyclopentadienyl)iron(II) [18] were prepared by published methods.

*$[R$-$(R^\star,R^\star)]$-$(+)_{589}$-Acetonitrile(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate (**1**)*

The preparation of this complex is based upon the method used by Treichel et al. to prepare similar compounds [19]. Thus, bromodicarbonyl(η^5-cyclopentadienyl)-iron(II) (2.0 g, 7.8 mmol) and $[S$-$(R^\star,R^\star)]$-(+)-1,2-phenylenebis(methylphenylphosphine) (2.52 g, 7.8 mmol) were suspended together in acetonitrile (50 ml) and the mixture was irradiated with a 125 watt Hanovia lamp for 30 min. The resulting deep brown solution was then reduced in volume to ca. 20 ml and treated with a solution of NH_4PF_6 5 g (31 mmol) in water (20 ml). Diethyl ether (100 ml) was added to this mixture, which was then stirred for ca. 12 h. A brick-red precipitate of the desired product separated. This was filtered off, washed with diethyl ether, and recrystallized from hot methanol: red prisms, m.p. 230–321°C (dec); 4.6 g (94%); $[\alpha]_{589}$ $+419°$ (c 0.224, CH_2Cl_2). Anal. Found: C, 51.6; H, 4.5; N, 2.3; P, 14.9. $C_{27}H_{28}F_6FeNP_3$ calc: C, 51.5; H, 4.5; N, 2.2; P, 14.8%. ^{1}H NMR: δ 1.70 (t, 3H,

^5J(PH) 1.3 Hz, NC*Me*), 2.10 (d, 3H, ^2J(PH) 10.2 Hz, PMe), 2.34 (d, 3H, ^2J(PH) 9.2 Hz, PMe), 4.17 (t, 5H, ^3J(PH) 1.5 Hz, C_5H_5), 7.20–7.84 (m, 14H, aromatics).

[R-[(R),(R*,R*)]-(+)$_{589}$-(η^5-Cyclopentadienyl)methylphenylarsine-[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ((R_{As})-2)*

A mixture of **1** (2.0 g, 3.2 mmol) and (±)-methylphenylarsine (0.53 g, 3.2 mmol) in methanol (20 ml) was stirred for 2 h under reflux. The clear orange solution was then cooled to room temperature and diluted with diethyl ether (50 ml). The product separated during ca. 12 h as yellow needles, m.p. 230–232 °C dec; 2.1 g, (88%); $[\alpha]_{589}$ +294° (*c* 0.232, CH_2Cl_2). Anal. Found: C, 50.7; H, 4.4; P, 12.7. $C_{32}H_{34}AsF_6FeP_3$ calc: C, 50.8, H, 4.5; P, 12.3%. ^{1}H NMR: δ 0.58 (d, 3H, ^3J(HH) 5.3 Hz, AsH*Me*Ph), 1.83 (d, 3H, ^2J(PH) 9.0 Hz, PMe), 2.28 (d, 3H, ^2J(PH) 8.2 Hz, PMe), 3.28 (m, 1H, As*H*MePh), 4.34 (t, 5H, ^3J(PH) 1.8 Hz, C_5H_5), 7.05–7.92 (m, 19H, aromatics).

[R-[(R),(R*,R*)] / [R-[(S*)(R*,R*)]-(η^5-Cyclopentadienyl)methylphenylarsino[1,2-phenylenebis(methylphenylphosphine)]iron(II) ((R_{As})-3 / (S_{As})-3)*

The complex (R_{As})-**2** (0.20 g, 0.26 mmol) was added to a solution of KOBu^t (0.15 g, 1.34 mmol) in tetrahydrofuran (20 ml) at −65 °C. After ca. 10 min stirring, the red solution was evaporated to dryness and the residue was dissolved in toluene (at 20 °C). The extract was filtered, the solvent removed from the filtrate, and the residue recrystallized from tetrahydrofuran-n-hexane to yield deep orange crystals of the product: m.p. 232 °C dec, 0.14 g (88%). Anal. Found: C, 63.1; H, 6.0; P, 9.3. $C_{32}H_{33}AsFeP_2$ calc: C, 63.4; H, 6.1; P, 9.1%. ^{1}H NMR (toluene-d_8): δ 0.68 (s, 3H, AsMe-major), 1.74 (s, 3H, AsMe-minor), 2.06 (t, 3H, $|^2J(PH)| + |^4J(PH)| = 7.7$ Hz, PMe-major), 2.06 (t, 3 H, $|^2J(PH)| + |^4J(PH)|$ ca. 8 Hz, PMe-minor), 2.10 (t, 3H, $|^2J(PH) + |^4J(PH)| = 8.0$ Hz, PMe-minor), 2.16 (t, 3H, $|^2J(PH)| + |^4J(PH)| = 8.1$ Hz, PMe-major), 3.95 (t, 5H, $^3J(PH) = 1.5$ Hz, C_5H_5-minor), 4.08 (t, 5H, $^3J(PH) = 1.3$ Hz, C_5H_5-major), 6.94–8.10 (m, 38H, aromatics-major, minor). In toluene-d_8 at 293 K (R_{As})-**2** (major)/(S_{As})-**2** (minor) = 2/1.

[R-[(S),(R*,R*)]-(+)$_{589}$-(η^5-Cyclopentadienyl)ethylmethylphenylarsine-[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ((S_{As})-4)*

The complex (R_{As})-**2** (1.0 g, 1.32 mmol) was added to a solution of KOBu^t (0.74 g, 6.60 mmol) in tetrahydrofuran (50 ml) at −65 °C. After ca. 10 min an excess of iodoethane (0.53 ml, 6.60 mmol) was added to the cold solution. The mixture was then warmed to room temperature and the solvent and the excess of ethylating agent were evaporated off. The residue was extracted into dichloromethane and this solution was washed, first with water and then with a solution of NH_4PF_6 (2 g, 12.3 mmol) in water (10 ml). The organic layer was then dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was dissolved in a small quantity of dichloromethane and the solution was passed through a column of neutral alumina containing 10% water. The filtrate, upon concentration and dilution with diethyl ether, yielded orange prisms of the product: m.p. 230–232 °C dec; 0.9 g (87%), $[\alpha]_{589}$ +403° (*c* 0.200, CH_2Cl_2). Anal. Found: C, 51.7; H, 4.7; P, 12.2. $C_{34}H_{38}AsF_6FeP_3$ calc: C, 52.1; H, 4.9; P, 11.9%. ^{1}H NMR: δ 0.54 (s, 3 H, AsMe), 0.72 (t, 3H, ^3J(HH) = 7.6 Hz, AsCH$_2$*Me*), 1.30 (m, 1H, AsC*H*HMe), 1.62 (m, 1H, AsCH*H'*Me),

2.14 (d, 3H, ^2J(PH) = 8.6 Hz, PMe), 2.42 (d, 3H, ^2J(PH) = 9.2 Hz, PMe), 4.17 (t, 5H, ^3J(PH) = 1.8 Hz, C_5H_5), 6.95–7.11 (m, 19H, aromatics).

[R-[(R),(R*,R*)]-(+)$_{589}$-(η^5-Cyclopentadienyl)ethylmethylphenylarsine[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ((R_{As})-4)*

A mixture of **1** (2.0 g, 3.2 mmol) and (±)-ethylmethylphenylarsine (0.62 g, 3.2 mmol) in methanol (50 ml) was heated under reflux for 2 h. The clear orange solution was then evaporated to dryness and the residue was fractionally crystallized from dichloromethane/diethyl ether and from acetone. The first crop of almost pure (R_{As})-**4** was obtained by diluting the initial dichloromethane extract with diethyl ether. After the crystals of this diastereomer were separated, the mother liquor was taken to dryness and the residue was extracted with hot acetone (500 ml). The acetone extracted mainly (S_{As})-**4**, which crystallized when the solution was concentrated to ca. 50 ml. The acetone-insoluble material was found to be a 1/1 mixture of (R_{As})- and (S_{As})-**4**, which was again dissolved in dichloromethane and diluted with diethyl ether. After three cycles of this procedure, and a final recrystallization of the combined fractions of (R_{As})-**4** from dichloromethane/diethyl ether, the total yield was 1.1 g (44%); m.p. 232–234°C; $[\alpha]_{589}$ +359° (*c* 0.214, CH_2Cl_2). Anal. Found: C, 52.4; H, 5.2; P, 11.7. $C_{34}H_{38}AsF_6FeP_3$ calc: C, 52.1; H, 4.9; P, 11.9%. ^{1}H NMR: δ 0.55 (t, 3H, ^3J(HH) = 6.2 Hz, $AsCH_2Me$), 0.68 (m, 1H, AsC*H*H′Me), 1.06 (s, 3H, AsMe), 1.21 (m, 1H, AsCH*H*′Me), 2.12 (d, 3H, ^3J(PH) = 7.4 Hz, PMe), 2.28 (d, 3H, ^2J(PH) = 7.7 Hz, PMe), 4.18 (t, 5H, ^3J(PH) = 1.8 Hz, C_5H_5), 6.83–8.01 (m, 19H, aromatics). Recrystallization of the combined crude (S_{As})-**4** from hot acetone yielded the pure enantiomer: M.p. 232–234°C; 1.0 g (41%); $[\alpha]_{589}$ +402° (*c* 0.199, CH_2Cl_2). ^{1}H NMR: identical to material obtained by asymmetric synthesis.

(R)-(−)$_{589}$-Ethylmethylphenylarsine

Pure (S_{As})-**5** (2.0 g, 2.6 mmol) was suspended in methanol (100 ml) and KCN (1.7 g, 26 mmol) in water (10 ml) was added. The mixture was heated under reflux for 5 days, and the solvents were then removed by distillation. The residue was extracted into dichloromethane, and the extract was washed with water, dried over $MgSO_4$, and was evaporated to dryness. The residue was extracted with petroleum ether b.p. 40–60°C (50 ml). The petroleum contained the optically active tertiary arsine, which remained after the solvent was removed (0.15 g, 30%); $[\alpha]_{589}$ −2.0° (*c* 0.751, Et_2O) {Lit.: $[\alpha]_{589}$ −3.05° (*c* 0.369, Et_2O) [20]}. The petroleum-insoluble material was chromatographed on neutral alumina containing 10% water with dichloromethane as eluent to give two fractions. The first fraction contained unchanged (S_{As})-**4** (0.6 g, 30%); the second fraction contained the new compound [*R*-(*R**,*R**)]-(+)$_{589}$-cyano(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) (**8**) which was isolated as yellow needles from dichloromethane/diethyl ether: m.p. 285–287°C dec; 0.79 g (66%); $[\alpha]_{589}$ +252° (*c* 0.230, CH_2Cl_2). Anal. Found: C, 66.2; H, 5.0; N, 2.9; P, 13.0. $C_{26}H_{25}FeNP_2$ calc: C, 66.6; H, 5.4; N, 3.0; P, 13.2%. ^{1}H NMR: δ 2.01 (d, 3H, ^2J(PH) = 7.7 Hz, PMe), 2.38 (d, ^2J(PH) = 9.7 Hz, PMe), 4.14 (t, 5H, ^3J(PH) = 1.5 Hz, C_5H_5), 7.10–7.85 (m, 14H, aromatics). IR(Nujol): 2061 cm^{-1} (ν(CN)).

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